Thermally Stimulated Current Study on Flexible Siloxane-Modified Epoxy Sheets

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Abstract: Copolymers prepared from the epoxy resin of ALBIFLEX and PMPs oligomer were evaluated with IR, 1H- and 13C NMRs for structural determinations. The flexible epoxy resin as a model compound was examined by TSC with variations on the operational parameters t_p and V_p. Transitions denoted as T_g, T_g', T_g", T_g, and T_g, in increasing order of temperature were observed for these copolymers. As an example, ESAF-7430 copolymer showed these transitions at -138, -84, 26, 87, and 110 °C, respectively. Each transition except the T_g at 110 °C, has been correlated to a segment in the copolymeric structure. The result indicates that TSC provides clear molecular transitions at the temperature of the transition. The molecular transition of the grafted PMPS-siloxane segment in an epoxy matrix appeared at the -45 °C region as a broad, nearly flat peak as it filled the concave part of the TSC curve of the unmodified resin. The flexibility that the modified copolymers retained may be attributed to these sub-T_g transitions as observed in the TSC spectrum.

Keywords: TSC, Flexible siloxane-epoxy resin, Relaxation transition, T_g

Introduction

Epoxy resin as one of the engineering plastics has been known for its dimensional stability and is used rather extensively in high-tech applications [1-4]. However, epoxy resin often requires the addition of a toughening agent to offset its brittleness [5-10]. Epoxy resin modified with flexible PMPS has shown much impact improvement without the need of other toughening agents [5]. On the other hand, a flexible epoxy resin of ALBIFLEX 108 (A 108) processes a T_g lower than the temperature needed for our application [6]. The modification on this A 108 was needed and was conducted with the addition of a dihydroxyarenes such as BPA to generate a hydroxyl group as a reaction site for the condensation with methoxy-terminated PMPS. The resultant PMPS-modified epoxy resins, abbreviated as ESAF copolymers, were examined using thermally stimulated current (TSC) for sub-T_g transitions.

The purpose of this investigation is to study the molecular transition of the flexible epoxy resins with testing runs over the variable operational parameters of the TSC to obtain precision data [11-14]. Copolymers prepared from the flexible epoxy resin of A 108 with PMPS oligomer were also examined with the TSC technique for their thermal relaxation transitions.

Experimental

1. Materials

ALBIFLEX 108 (A 108) epoxy resin was purchased from Hanse Chemie GmbH. It has an epoxide equivalent weight (EEW) of 210-230 g/mole. DC-3074, Poly(methylphenyl)siloxane (PMPS) containing Si-phenyl/Si-CH_3 in 50/50 ratio was donated by Dow Corning Co., Taiwan. 4,4'-Isopropylidene-diphenol (Bisphenol A, BPA) from Acros Co., 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) from Anchor Chem Co., and tetraisopropyl titanate (TPT) from Du Pont Co., were used directly.

2. Preparation of epoxy copolymers (BPA-A 108 & ESAF)

(1) Preparation of BPA-A 108 copolymer

A hot melt method was used in this preparation [5-8]. BPA-A 108 epoxy resin was prepared with the addition of BPA to the A 108 in one to two molar ratios with the temperature maintained at 120-130 °C. The product was washed with toluene to remove the un-reacted BPA. The final product was dried in vacuum at 60 °C for 24 hrs. The EEW was...
found to be in the range 542 to 556 g/mole. The infrared (IR) spectrum of the product (cast on the NaCl plate) exhibited absorptions of -OH at 3420 cm⁻¹, [-C(CH₃)₂-phenyl] at 1379 cm⁻¹, (Si-O-C) at 1176 cm⁻¹, (Si-O-Si) at 1107-1033 cm⁻¹, and oxirane at 911 cm⁻¹. The ¹H NMR spectrum in ppm (CDCl₃) of the copolymer showed peaks (δ) of [-C(CH₃)₂-phenyl-] at 6.85 to 7.10, [-CH₂-phenyl-] at 6.84 to 7.12, [oxirane for -O-CH₂] at 2.71, 2.87, [oxirane for -O-CH₂] at 3.32, and [-C(CH₃)₂-phenyl-] at 1.62. The ¹³C NMR spectrum in ppm (CDCl₃) showed a main peak (δ ppm) of [-CH₂-phenyl-] at 35.15, [oxirane] at 44.60, 50.21, [-C(CH₃)₂-phenyl-] at 41.66, [-C(CH₃)₂-phenyl-] at 30.99, and [-C(CH₃)₂-phenyl-] at 113.92, 127.72, 143.66, and 156.10.

(2) Preparation of ESAF-74X copolymers
BPA-A 108 was added with pre-measured DC-3074 to a flask with a stirrer [5, 6]. The reaction temperature was raised and maintained at 130 °C for 2-3 hrs. The ESAF-74X was denominated for the DC-3074 siloxane-modified BPA-containing A 108 epoxy resins where X is the weight increment of DC-3074, and in 10, 20, and 30 wt% to BPA-A 108 for ESAF-7410, -7420, and -7430 copolymers, respectively. The ESAF-system had an EEW of 678 for ESAF-7410, 713 for ESAF-7420, and 742 for ESAF-7430. The Infrared (IR) spectrum of ESAF-7430 (cast on NaCl plate) as an example exhibited absorptions at 3386 cm⁻¹ [-OH], 1289 cm⁻¹ [-Si-CH₃], 1376 cm⁻¹ [-C(CH₃)₂-phenyl], 1237 cm⁻¹ [-C-O-C], 1175 cm⁻¹ [-Si-O-CH₂], 1039, 1097 cm⁻¹ [-Si-O-], and 908 cm⁻¹ [oxirane]. The ¹H NMR spectrum (CDCl₃) showed major peaks (δ) at 7.65, 7.41 ppm [Si-phenyl], 6.90-7.25 ppm [-C(CH₃)₂-phenyl], 6.75 ppm [oxirane for (O-C-H)], 2.72, 2.88 ppm [oxirane for (O-C-H)], 1.63 ppm [-C(CH₃)₂-phenyl-], and 0.12 ppm [-Si-CH₃]. The ¹³C NMR spectrum with CDCl₃ showed peaks (δ) at 143.60, 129.54, 114.51, 156.08 ppm [-C(CH₃)₂-phenyl-], 41.66 ppm [-C(CH₃)₂-phenyl], 30.98 ppm [-C(CH₃)₂-phenyl], 115.59, 114.66, 156.08 ppm [-CH₂-phenyl-], 127.73, 129.54, 134.16, 134.01 ppm [-Si-phenyl], 1.00 ppm [Si-CH₃], 50.17 ppm [-Si-O-CH₃], and 44.61, 50.23 ppm [oxirane].

(3) Curing process of the siloxane-modified ESAF-74X copolymers
Epoxy resins of ESAF-74X series with an appropriate amount in 5-10 g were mixed with a curative and the curing procedures were conducted as follows. As a typical example, 2 wt% of amine curative (DMP-30) was added to the ESAF resin. The resin was well mixed and then degassed and placed in an aluminum or Teflon-coated sample holder, and then was placed at 120 °C for 1 hr and post-cured at 140 °C for 1 hr, if needed. The cured sample in sheets of 50 mm and 2 mm thickness were used for the TSC and DSC testing.

3. Characterizations
(1) Epoxy equivalent weight (EEW) measurements
HCl/pyridine was used for the EEW determination [15].
(2) DSC measurement
A Du Pont 9000 thermal analyzer coupled with a TA-2000 data analysis system with a heating rate of 10 °C/min under N₂ atmosphere was used for the Tg measurement.
(3) TSC measurement
A solomat TSC/RMA model 9100, Solomat Instrument Co., Stamford, CT, USA was used with the temperature range of -150 °C to 140 °C or 160 °C with a heating rate of 7 °C/min.
(4) Infrared (IR) measurement
The IR measurements were performed with a JASCO IR-700 spectrophotometer. The sample was prepared with the dissolved solution in acetone and cast on the NaCl plate. The solid sample was mixed in KBr and pressed into a KBr pellet.
(5) ¹H- and ¹³C NMR measurements
Structural data of the hydrogens and carbons with individual chemical shifts were measured with ¹H- and ¹³C NMR, respectively. The ¹H- and ¹³C NMR spectra were measured with a Bruker AM-300WB FT-NMR with the kind assistance of the NSC Instrument Lab.
(6) TSC measurements
Two procedures were used for the TSC measurements:
(i) The sample was polarized at constant Vp = 50 V/min and Tp = 80 °C, with polarization time (tp) in variation of 2, 5, 10, 20, 40, 80, and 150 mins. It was cooled quickly with Newtonian to a temperature To = -150 °C to freeze the oriented dipoles. After the sample was kept for 5 minutes at To to equilibrate it, the current due to dipole relaxation was measured using a picoammeter at a heating rate of 7 °C/min.
(ii) Samples were subjected to 5, 10, 20, 50, and 100 V/mm at Tp = 80 °C with polarization time tp = 10 min. The same procedures of freeze-in and thermal relaxation at 7 °C/min were followed.